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High-temperature membrane reactors: potential and problems

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Abstract

The most recent literature in the field of membrane reactors is reviewed, four years after an analogous effort of ours (Saracco et al., 1994), describing shortly the potentials of these reactors, which now seem to be well established, and focusing mostly on problems towards practical exploitation. Since 1994, progress has been achieved in several areas (sol–gel deposition of defect free sol–gel derived membranes, reduction in thickness of Pd membranes, synthesis of zeolite membranes) whereas stagnation was noticed in some others (high-temperature sealing of membranes into modules, scaling-up of membrane reactor, etc.). As a result, despite the still increasing research efforts, industrial application does not seem to be round the corner, yet. However, several non-permselective membrane reactor opportunities with currently available membranes might pave the way for more sophisticated applications. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Inorganic membrane reactor; Catalysis

1. Introduction

There has been a flourishing reviewing activity in the field of inorganic membrane reactors in recent years (e.g. Tsotsis et al., 1993; Saracco and Specchia, 1994, 1998b; Saracco et al., 1994; Armor, 1995; Dalmon, 1997). Almost an entire book was even dedicated to this topic (Hsieh, 1996), a clear sign of the massive interest of the scientific community in this topic. Most reviews were primarily aimed at showing the remarkable potential of membrane reactors, stressing possibilities and application opportunities and critically assessing the open literature. Today, the potential of membrane reactors is rather well assessed and as clear as the technological gap that still has to be filled in order to achieve industrial practice. This survey is therefore mainly focused on hurdles still standing on the way to large-scale application. However, new opportunities, much closer to viability, will also be considered.

Table 1 lists the major challenges for the success of inorganic membranes pointed out in 1994, together with

a qualitative assessment of the progress achieved in the meanwhile. The present communication will try to elucidate and quantify such progress and to identify the major issues still needing further research efforts. Three major areas of applications will be addressed, namely:

- (1) *Yield-enhancement of equilibrium-limited reactions:* a reaction product is selectively permeating through the membrane, thereby enhancing the per-pass conversion compared to conventional fixed-bed reactors (e.g. for dehydrogenations, Fig. 1a); coupling of reactions at opposite membrane sides has also been envisaged in this context (Fig. 1b);
- (2) *Selectivity enhancement:* accomplished by selective permeation (Fig. 1c) or controlled addition (Fig. 1d) of a reactant through the membrane;
- (3) *New emerging application opportunities:* a number of potential applications (membrane reactor with separate feed of reactants, catalytic filters and traps, slurry membrane reactor, etc.) were recently investigated, which do not require membrane perm-selectivity to gases and therefore appear to be closer to industrial success.

Polymeric membranes, often applied in bioreactor or liquid-phase applications (e.g. Gao et al., 1995), will not be considered hereafter. However, it is worth mentioning

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Table 1
Major challenges in the development of inorganic membrane reactors

Field/challenges	Progress from 1994	References
Materials science		
Synthesising defect-free and homogeneous membranes having pores of molecular dimensions ($<10 \text{ \AA}$).	+	Kapteijn et al. (1995), Coronas et al. (1998) and deVos and Verweij (1998)
Reducing the membrane thickness ($<10 \mu\text{m}$) so as to keep gas permeation acceptable.	+	deVos and Verweij, 1998
Reproducing the above results on large scale membranes.	—	Verweij (1998)
Addressing problems of brittleness for both ceramic and Pd-alloy membranes.	+	Shu et al. (1995) and Jeema et al. (1996)
Developing relatively cheap high-temperature sealing systems.	—	no particular progress since Velterop (1991)
Finding new materials with better properties than Pd, $\gamma\text{-Al}_2\text{O}_3$, Vycor glass, ...	\pm	Balachandran et al. (1995) and ten Elshof et al. (1995)
Catalysts science		
Developing new membrane catalysts less sensitive to poisoning or coking.	\pm	Edlund and Pledger (1994)
Getting a better control of the catalytic activation of ceramic porous membranes.	+	Yeung et al. (1994), Vitulli et al. (1997) and Szeigner et al. (1997)
Chemical engineering		
Understanding and modelling highly-selective transport mechanisms.	+	Krishna and van den Brooke (1995), Shelekin et al. (1995) and van den Graaf (1998)
Increasing the membrane area per unit volume.	+	Smid et al. (1996)
Developing complex modelling for large scale membrane reactor modules.	—	Perhaps it is too early to expect this, yet.
Developing technologies for heat supply and temperature control in large scale modules.	—	See above
Developing criteria for the choice of the optimal size of membrane reactors, of the flow patterns and of the number of stages/recycles/intermediate feeds.	—	See above

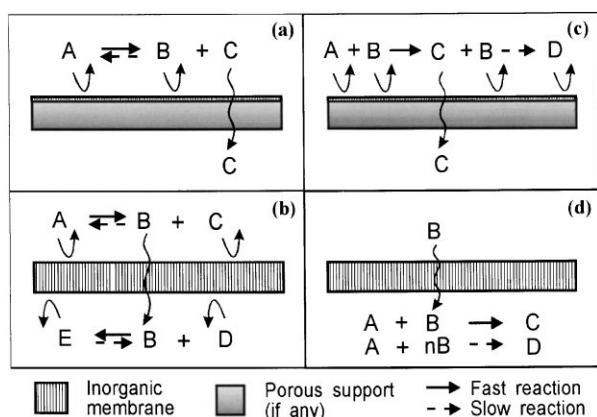


Fig. 1. Prevalent application opportunities of inorganic membrane reactors. Conversion enhancement with catalytic membrane reactors: (a) selective permeation of a reaction product of an equilibrium limited reaction; (b) coupling of reactions. Selectivity enhancement with catalytic membrane reactors: (c) selective permeation of an intermediate, desired product; (d) dosing a reactant through the membrane.

that polymeric membranes (mostly based on polyimides) are currently being considered for application in reactors with gas-phase reactions at temperatures up to 300°C (Tröger et al., 1997).

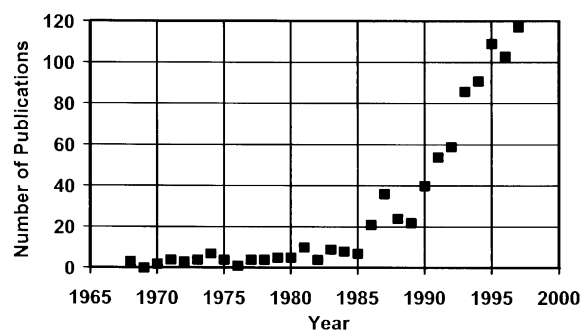


Fig. 2. Variation of the number of publications per year on catalytic membrane reactors since 1965 included in the Chemical Abstracts database.

Our paper is based on a database search, whose results are worthwhile commenting. For all years from 1965 to 1997, the Chemical Abstracts library was checked with the following keywords: CATALYTIC and MEMBRANE and REACTOR. The obtained number of publications per year was plotted in Fig. 2 vs. the year itself. The results enlighten a remarkable increase in the last decade which does not seem to have reached its peak, yet. From the authorship of these papers, it is clear that the membrane-reactor research community is not only

Table 2
Papers distribution per application type of catalytic membrane reactors in 1994 and 1997

Application field	1994 (%)	1997 (%)
Yield-enhancement of equilibrium reactions	50	35
Selectivity increase	30	50
Bioreactor applications	20	15

growing in number but also widening its territorial borders. New-comers from developing countries in Asia or Latin America are numerous. Particularly, researchers from the Republic of China have authored about 5% of the scientific papers in the field (e.g. Liu et al., 1997; Cao et al., 1997). Most of these studies are related to γ -alumina membranes which were extensively studied in Western countries a few years earlier (Saracco and Specchia, 1994). Further, the above papers are mainly addressed to equilibrium-enhancement concepts which are slowly being replaced by selectivity enhancement studies in Western countries. Table 2, whose figures were derived for 1994 and 1997, shows how in recent years the prevalent research field in the membrane reactors has shifted from equilibrium-circumvention exactly to selectivity-enhancement. The most likely reasons for this circumstance lie in the fact that partial-oxidations or hydrogenations have a much wider spectrum of industrial applications than dehydrogenations, and that membrane permselectivity is a less urgent need (if any) for this kind of applications.

The mentioned literature will be reviewed and discussed from an application-oriented viewpoint, rather than from a materials-oriented one. Two Sections (2 and 3, respectively) will be dedicated to the classical fields of equilibrium circumvention and selectivity enhancement, leaving to Section 4 the analysis of new emerging applications of membrane reactors. Those interested will find details on particular membrane materials (e.g. zeolites, solid-electrolites, Pd alloys) in Section 2.2.

2. Yield enhancement for equilibrium-limited reactions

2.1. Reactions and reactors

The most common application opportunity of membrane reactors lies in the circumvention of a chemical equilibrium so as to achieve higher per-pass conversions by selective permeation, through the membrane, of at least one of the reaction products (Fig. 1a).

The major potential candidates for such application of inorganic membrane reactors are dehydrogenations. Since these reactions are endothermic, conversion is

favoured at high temperatures at the price of significant occurrence of side reactions, which reduce selectivity and lead to catalyst deactivation by coking. By using a membrane reactor, equal conversions could be obtained at lower temperatures thereby suppressing undesired reactions. Further, since dehydrogenations imply an increase of the overall number of gas molecules of the system, they can be forced to high conversions by reducing the operating pressure, which entails comparatively high reactor volumes. Such volumes could be reduced using a membrane reactor, since, conversion being equal, higher operating pressures could be tolerated. Moreover, the permeated reaction product can be recovered in a quite pure form. However, if the membrane is not permselective enough, the conversion increase remains limited by the permeability of the reactants, which also affects the purity of the product.

Nevertheless, dehydrogenations have been studied, taking advantage of the small size of the hydrogen molecule or of special selective transport mechanisms, by using either porous (e.g. porous alumina, Vycor glass) or dense membranes (e.g. Pd alloys, SiO_2 , proton-conductive solid electrolytes, etc.).

Fig. 1b shows a further intriguing application opportunity: the coupling of reactions at the opposite membrane sides. A typical case study is the contemporary handling of a dehydrogenation (endothermic) and a hydrogenation (exothermic) at the two sides of a Pd membrane permeated by hydrogen; this operation mode could enhance the per-pass conversion of both reactions. Furthermore, the exothermic reaction could in principle supply the heat required for the endothermic one. Despite these potential benefits, little experimental study has been addressed to this last topic in recent years. Further, the number of degrees of freedom which can be used for control purposes is decreased compared with the single-reaction mode. Experiments proving the reaction coupling concept were recently performed by Gobina and Hughes (1996a) and by Itoh and Wu (1997). The first researchers carried out an experimental and modelling study of the catalytic dehydrogenation of *n*-butane. The use of nitrogen, CO/N_2 , O_2/N_2 sweep gases at the opposite membrane side allowed to increase conversion up to 5–8 times the equilibrium value calculated on the basis of the reactant inlet concentration (5%), the largest values occurring due to reaction coupling of the permeated hydrogen with O_2 and CO. Itoh and Wu (1997) focused on the thermal sustainment played by the oxidation of the permeated hydrogen on the endothermic cyclohexane dehydrogenation occurring at the opposite membrane side; considerable energy savings compared to indirect heating of the reactor were proved.

In 1994, we reviewed a considerable amount of equilibrium reaction tests performed on available inorganic membranes in order to prove the potential of this reactor concept (Saracco and Specchia, 1994). As the principle of

equilibrium shift by membranes is now well established, since then, the number of reaction studies in the field has diminished. In this context, studies on dehydrogenations of alkanes and aromatic compounds have still received most attention (see e.g. those performed on Pd membranes: Gobina et al., 1995; Gobina and Hughes, 1996b; Sheintuch et al., 1997; Shu et al., 1997). Attention has also been paid to the steam- and CO₂- reforming of methane to syngas, led to high per-pass conversions by selective permeation of hydrogen through Pd–Ag membranes (Shu et al., 1995). Other reactions fields investigated are related to methane partial oxidation to syngas (Santos et al., 1995), to the water–gas-shift reaction (Ettouney et al., 1996) and to the reforming of methane or small hydrocarbons into higher hydrocarbons and hydrogen (Ali and Baiker, 1996; Kusakabe et al., 1996; Garnier et al., 1997). Finally, the investigations performed by Ali and coworkers on methylcyclohexane to toluene dehydrogenation in Pd-membrane-enclosed fixed-bed catalytic reactors are worth mentioning, since they entailed a conversion of nearly 80% (4 times higher than equilibrium), after 300 h, when operating at 0.5–2 MPa, 573–673 K and space velocities (referred to the reactor volume) of 2–12 h⁻¹ (Ali et al., 1995; Ali and Rippin, 1995; Ali and Baiker, 1997).

An interesting issue was pointed out by Tiscareño-Lechuga et al. (1996) in their study on ethylbenzene and cyclohexane dehydrogenation over a fixed-bed reactor enclosed in a porous alumina membrane reactor, using nitrogen as a sweep gas at the outside of the membrane for the removal of the permeation products. Their modelling proved that the higher-than-equilibrium conversions were primarily to be attributed to dilution of the reacting gases by the sweep gas permeating through the membrane, rather than to selective permeation of products.

Finally, several environmental-related reactions were attempted by using permselective membrane reactors. Ammonia decomposition into nitrogen and hydrogen from coal gasification streams was successfully tested by Collins and Way (1994) over Pd–Ag membranes. The measured conversion at 823 K in a membrane enclosed fixed-bed reactor of a Ni–Al₂O₃ catalyst was 79% instead of 17%, measured for a standard reactor. Similar results were obtained for other high-temperature decompositions of noxious gases such as H₂S by selective permeation of hydrogen through Pt–V membranes (Edlund and Pledger, 1994).

Some interesting studies were recently carried out to assess the role of catalyst distribution inside inorganic membrane reactors either inside the separative membrane or in the pellets belonging to a fixed-bed enclosed at the shell of at the tube side of tubular membrane. Some researchers at Notre Dame University (Yeung et al., 1994) performed a modelling study concerning the optimisation of the catalyst distribution in a catalytic

membrane where a first-order reaction occurs (e.g. dehydrogenation). Their conclusions were rather simple: a Dirac-delta function of the concentration of the catalyst in the membrane, placed at the feed side, allows the highest conversions. In other words, it is better to promote the reaction as close to the membrane as possible (on its surface) letting the rest of the membrane work as a mere separator of some of the reaction products. In case the local catalyst amount cannot overpass a given limit (as in all real cases), the optimal catalyst distribution turns to be a multiple step function, which tends to the Dirac delta function as long as the above limit is increased. Such step concentration profile can be obtained through tailored techniques (e.g. Vitulli et al., 1997). By the way, further studies at Notre Dame (Szegner et al., 1997) pointed out, from both an experimental and a theoretical point of view, how catalyst distribution effects within the pellets of a packed-bed enclosed in a inert membrane reactor can also affect the overall reactor performance, by using ethane dehydrogenation over Pt supported catalysts as a test reaction. As expected, the reactor performance was maximised when the catalyst was placed on the outer shell of the pellets and when permeation of reactant through sol-gel derived alumina membranes was kept low enough without decreasing too much hydrogen permeation.

2.2. Improvements in membrane permselectivity

All the above-mentioned membrane reactor studies further enlightened possible application opportunities but also strengthened the consciousness that the available membranes are not permselective enough to guarantee the success of this new technology. Besides, permselectivity has to be coupled with high enough permeability so as to avoid large areas of expensive membranes. Thermal stability of the membrane is then a further important issue to consider. As stated in 1994 (Saracco et al., 1994) “...there is no need to continue studying new reactions on currently available membranes...”. The major aim of membrane reactor studies in the well known field of dehydrogenation should be to check membrane stability under practical operating conditions, thus pointing the way to the still required improvements in membrane quality and performance.

Four major fields are being studied for the preparation of permselective, stable and permeable membranes:

- (1) modification of currently available membranes through e.g. deposition of highly permselective top layers by sol-gel, CVD, etc.;
- (2) synthesis of zeolite membranes;
- (3) synthesis of thinner and thinner Pd-alloy membranes;
- (4) development of membranes based on ion conductors.

2.2.1. Current membrane production and modification by permselective topayers

Industrial inorganic membranes are prepared through a variety of techniques (particle dispersion and slip-casting, sol-gel processes, phase separation and leaching, pyrolysis, anodic oxidation, etc.) and commercialised by a number of multinational companies (US Filters/SCT, NGK, Du Pont, Asahi Glass, TDK, Fujii Filters, etc.). Most current applications concern the filtration of gaseous or liquid streams in comparatively harsh environments. None of the industrially produced membranes enables sufficient permselectivity for gas molecules. The lowest pore size achieved reliably is about 5 nm for some γ - Al_2O_3 porous membranes manufactured by US Filters mostly for research purposes. Molecules are separated through these membranes only via a Knudsen diffusion mechanism, leading to permeation fluxes inversely proportional to square root of the molecular weight. Higher permselectivities could be obtained by modifying these membranes through suitable techniques (point 1 above).

A possibility lies in the further deposition of a SiO_2 top-layer on the available membrane through sol-gel techniques. By use of polymeric sols, de Lange et al. (1995) deposited a 60–100 nm porous silica layer upon mesoporous alumina membranes. Such top-layer (pore size < 1 nm) enabled molecular sieve-like separation factors in the order of 50–200 for H_2/CH_4 , well above the Knudsen value of 2.8. No details were though given concerning the long-term stability of these membranes.

Raman and Brinker (1995) tested a rather new approach for the synthesis of molecular sieving silica membranes. Hybrid organic-inorganic polymers prepared by co-polymerisation of tetraethoxysilane (TEOS) and methyltriethoxysilane were deposited on commercial alumina membranes. Through suitable heat treatments the inorganic matrix was densified and the methyl ligands pyrolysed. Rather interesting CO_2/CH_4 separation factors were thus achieved (up to 71) with a reasonable permeability ($2.57 \times 10^{-3} \text{ cm}^3/\text{cm}^2/\text{s}/\text{cmHg}$).

The most interesting results in the field of sol-gel derived silica membranes were though recently obtained by Verweij and coworkers (de Vos and Verweij, 1998) at Twente University. Their basic intuition was that most of the defects arising in the sol-gel derived membranes originate from dust particles present in the environment in which the membranes are produced. Normal laboratory air contains about 10^6 particles per cubic foot (class 1,000,000). Such particles statistically do interfere with the deposition steps of the sol-gel membranes eventually leading to the formation of defects which affect membrane permselectivity. Clean rooms of class 1000, with sections of class 10 were set up by these authors and the deposition of 30 nm-thick silica membranes was accomplished via a sol derived from hydrolysis of TEOS upon a flat support made of an α -alumina disk covered with two layers of γ -alumina. The obtained results are

rather surprising: H_2/CH_4 separation factors above 500 at 200°C with a hydrogen permeance of $2 \times 10^{-6} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ were achieved against values of 43 and 1.6×10^{-6} , respectively, previously obtained in non-clean rooms (Weyten et al., 1997). Further improvements are still possible. For instance, if porous silica membranes were made with a thickness of about 1 nm, H_2 permeance of $> 5 \times 10^{-5} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ could be realised provided no support and surface transfer rate limitations occur, even if, as admitted by the Authors, membrane sensitivity to water needs to be decreased. This may be achieved by chemical treatment of the internal silica surface (facing the γ -alumina support layer). Studies concerning the steam reforming of methane and propane dehydrogenation are currently in progress using the developed membranes. Much better results are expected compared to those obtained in earlier studies on silica membrane reactors (Weyten et al., 1997) in which yield increase compared with conventional packed-bed reactors has always been moderate owing to permselectivity or permeability problems. Of course, clean rooms are expensive. However, they are widely employed in the electronic industry.

Chai et al. (1994a) studied the improvement of the thermal stability of sol-gel derived γ - Al_2O_3 membranes. By adding La_2O_3 or BaO precursors to the basic alumina sol, a certain stabilisation of the pore structure could be obtained as a consequence of the inhibiting action of the above oxides towards sintering. The achieved pore sizes (> 3 nm) were in any case too high to enable permselectivities of practical interest.

A different approach consists in the reduction of the pore size of basic membranes by deposition of additional material within the pores themselves. Morooka et al. (1995) plugged the pores of a basic α -alumina tube (average pore size: 150 nm) by thermal decomposition of TEOS vapours fed in nitrogen flow to the membranes, kept in an oven at about 650°C. H_2/N_2 separation factors as high as 1000 were measured for the obtained membranes, which moreover showed good resistance to temperature cycling. In this context, Chai et al. (1994b) obtained a remarkable promotion of both hydrogen permeability and permselectivity through γ - Al_2O_3 membranes, by depositing inside the membrane noble metals such as Pt, Ru, Rh and Pd. Particularly, the H_2/N_2 separation factors obtained, exceeded the Knudsen values. By using these membranes, methane steam reforming could be driven to conversions twice as large as under equilibrium conditions in the temperatures range 300–500°C.

Gavalas and co-workers (e.g. Kim and Gavalas, 1995) obtained similar results by depositing SiO_2 within the pores of a Vycor glass membrane through a chemical vapour deposition technique. Silica deposition arose from reaction between SiCl_4 and H_2O , which were forced to pass through the pores of the support tube at

temperatures ranging from 600°C and 800°C. By keeping the deposit well inside the structure of the Vycor tube a mechanically stable membrane, also showing good resistance to thermal fatigue, could be produced. However, annealing at high temperatures promotes a silica densification process which leads to very low permeance. This problem is even worsened by the presence of water vapour. Besides, pore plugging intrinsically leads to low permeabilities since only the membrane original porosity can be filled with the molecular-sieve material providing gas-separation.

2.2.2. Zeolite membranes

A preferable approach would rather be the synthesis of membranes entirely characterised by a molecular sieve structure, i.e. zeolite membranes. Apart from their ability to discriminate molecules depending on their size, zeolite membranes are supposed to exhibit high thermostability, a essential feature for practical membrane reactor application. Moreover, the large variety of zeolite types should provide a tailor-made separation tool for specific applications. Zeolite properties can be adjusted by varying the Si/Al ratio or by cation-exchange, which make them promising for use as catalytic membranes. Further, the crystallinity of zeolite membranes ensures a well-defined pore structure, which is quite difficult to obtain when preparing molecular-sieve membranes from amorphous materials. Research efforts on zeolite membranes can be divided into three areas:

- (1) *Zeolite particles embedded in polymeric materials* (e.g. Zimmermann et al., 1997): these membranes are indeed gas-tight and have proven success for pervaporation applications (e.g. separation of ethanol–water mixtures; Gao et al., 1996). However, they are of no practical interest in the field of catalytic membrane reactors due to the low thermal resistance of the polymer matrix.
- (2) *Unsupported zeolite membranes*: these were the first inorganic membranes on which molecular sieving effects were observed by Haag and Tsikoyiannis (1991). A separation factor of 17 was obtained for the mixture *n*-hexane/2,2-dimethylbutane. However, permeability was rather low, which could be improved by developing supported zeolite membranes.
- (3) *Supported zeolite membranes*: this is the field where most hopes of industrial success are cultivated nowadays. The two most promising techniques are deep coating (Vroon, 1995), followed by filling up the pores remaining after heat treatment, or in situ crystallisation (Geus et al., 1992) in such a tight way to avoid defects.

The ultimate goal would be the synthesis of a defect-free single-crystal membrane, which would allow the lattice pores to control the separation process according to a molecular sieve mechanism. This objective appears nowadays unrealistic. The only zeolite membranes suc-

cessfully produced until now are made of silicalite-1 crystals grown together in such a tight way that the intergranular spacings do not affect the separation to a significant extent (Kapteijn et al., 1995). Such membranes were though only obtained at a lab-scale (a few-cm disks) on either stainless-steel or alumina supports.

Rather recently Noble and Falconer demonstrated the first evidence of a dense, defect-free, zeolite membrane in a tubular configuration (Coronas et al., 1997a,1998). These membranes have been cycled between ambient temperature and 500°C without any evidence of mechanical cracking.

Further, despite the comparatively low pore size of the silicalite-1 zeolite (5.2–5.5 Å), the obtained separation factors (e.g. 12.8 for H₂/SF₆ at 583 K; Noble and Falconer, 1995) should still be improved, possibly by the synthesis of membranes made of zeolites with smaller pores than those of silicalite-1. An outstanding review of all the attempts already made in this direction was recently written by van de Graaf et al. (1998).

2.2.3. Dense metal membranes

Pd-alloy membranes have always been the most studied dense membranes, due to their comparatively high hydrogen permselectivity. As a shortcoming, they suffer from brittleness after repeated thermal cycling owing to the transition between its α - and β - phases, stable at low and high temperatures, respectively (Armor, 1995). This problem can be overcome or, at least, reduced by the use of some alloying elements (e.g. Ag, Ru, Rh), which stabilise the β -phase against the α -phase.

Poisoning by CO and sulphur compounds, present in a number of gas streams, remains though a serious problem affecting both the permeability and the catalytic properties of Pd-alloy membranes, limiting their practical applicability. At *Bend Research Inc.* (Bend - OR) new membranes are being developed and applied (H₂S decomposition; Edlund and Pledger, 1994), on the basis of composite structures of different metals (Pt, V), which are less sensitive to poisoning. Since the permeability of these membranes is much lower, they cannot be considered as a real breakthrough, yet. It should be realised however that, for reactions like H₂S decomposition, Pd membranes cannot be used since they are reported to fail by catastrophic rupture within seconds of exposure to pure H₂S at 973 K.

Most research in this area is devoted to the reduction of the thickness of supported Pd-alloy membranes so as to enable high enough permeabilities. This should obviously be achieved while avoiding any formation of pinholes, cracks or other defects which would considerably lower membrane permselectivity.

Electroless plating was recently employed by Varma and coworkers (Yeung and Varma, 1995) to synthesise Pd and Pd–Ag thin membranes on various supports (e.g. porous alumina, Vycor glass). These membranes were

a few microns thick and showed good mechanical and thermal stability provided particular procedures had been followed. In fact, by appropriate use of the osmotic pressure during conventional electroless plating with typical hydrazine baths, the microstructure and thickness of the metal could be systematically manipulated.

Bauxbaum and Kinney (1996) employed the electroless plating technique to form thin Pd layers on tantalum and niobium tubes. The main transport resistance was in the refractory metal substrate. The cost of such membranes was \$45/ft of 3/8-in tubular membrane, and the hydrogen permeability through these membranes was $0.00147 \text{ mol/m}^2\text{/s/Pa}^{1/2}$ at 420°C . On the basis of such data and assuming durability is at least 1 year, competitive application of such membranes could be accomplished for hydrogen recovery in petrochemical plants or for membrane reactors.

Jeema et al. (1996) deposited Pd membranes over a metal support cheaper than tantalum or niobium: porous stainless steel. The use of a metal support entails lower problems of thermal expansion mismatch between membrane and support and avoid brittleness. These authors could keep membrane thickness at just $6 \mu\text{m}$ with no defects affecting hydrogen permeability. However, the surface quality of commercial stainless steel tubes did not allow the above results unless a preliminary shot-peening treatment was performed to modify their surface pore size. Higher thickness ($8.5\text{--}12 \mu\text{m}$) and, consequently, lower permeability were obtained once again by electroless plating by Ilias et al. (1997) over $\alpha\text{-Al}_2\text{O}_3$ supports.

Another interesting technique for the deposition of ultrathin ($< 500 \text{ nm}$) Pd membranes on ceramic supports is magnetron sputtering. Jayaraman et al. (1995) found that two main parameters are the most critical in this context: surface roughness of the substrate and deposition temperature. For instance, well-adhered Pd films could be deposited on sol-gel derived γ -alumina porous substrates but not on coarse α -alumina ones. Further, this could not be achieved by operating at room temperatures, but only above 80°C . The above sputtered membranes are perhaps the thinnest Pd membranes ever produced, however N_2 -tightness was never achieved and the technique employed is hardly suitable for large-scale production.

2.2.4. Solid electrolytes/mixed conductors

It is finally worth mentioning that some interest arose in recent years concerning solid electrolyte membranes based on proton conductors or on oxygen conductors (e.g. perovskites; Itoh et al., 1994). As opposed to Pd-alloy membranes, solid electrolytes show generally a good thermochemical stability, but their permeability is very low unless rather high temperatures are employed ($> 800^\circ\text{C}$). The potentials offered by new perovskites, showing comparatively higher permeabilities than the

classical doped- ZrO_2 , have still to be fully explored. Most membranes synthesised until now in this last context are indeed unsupported (Pei et al., 1995), which entails a rather high mechanical stability but rather low permeability. The possibility of reliably depositing thin and stable films on porous supports has only been attempted in rare cases and with unsatisfactory results, so far, especially due to the occurrence of cracking during the drying and/or heat treatment steps of the preparation procedure. Most applications studied with this kind of membranes regard selectivity enhancement in partial oxidation reaction. Particularly, remarkable studies are being carried out by either academic or industrial researchers on perovskite membranes in the fields of methane to syngas conversion (Balachandran et al., 1997) and the oxidative coupling of methane (Balachandran et al., 1995). Further discussion on the stability and performance of such membranes is provided in Sections 3.1 and 3.2.

2.3. Increasing the specific membrane area

Independent of the membrane specific nature, the major identified hurdles preventing a wide spread application of ceramic membranes are the complex and expensive preparation and the relative low specific area's obtained with existing module techniques. However, improved concept and production techniques have become available in recent years leading to ceramic hollow fibre modules with potential surface to volume ratios in modules larger than $1000 \text{ m}^2/\text{m}^3$, but what is the specific area requested for a typical membrane reactor application? The answer will strongly depend on the specific application, but for non-permselective membranes where diffusional resistance in the ceramic membranes will be roughly in the same order as in the catalyst particles, the presently available membrane tubes of a diameter of say $5\text{--}30 \text{ mm}$ will probably be sufficient. If selective transport is required, or intensification of the process operation is aimed at, one or two orders of magnitude smaller tubes would be welcome, especially if a similar decrease in cost per m^2 membrane area is achieved.

As an example of the progress made towards cheap and large-area modules of ceramic hollow fibre membranes, we will take the results obtained by TNO in the Netherlands (Smid et al., 1996). A hollow fibre precursor is produced via a spinning process from a mixture of an inorganic material and a polymer binder. Then the fibre precursor is heated at high temperature in an inert atmosphere or air to produce the inorganic hollow fibre itself. A successful product should fulfil the following requirements: simple production methods; good control of diameter, length, and wall thickness; control of porosity; control of pore diameter distribution; sufficient mechanical strength.

Table 3
Properties of the ceramic hollow fibre membranes produced by TNO (Brinkman, 1998)

<i>Structure</i>	
Materials	Al ₂ O ₃ , Si ₃ N ₄ , SiC, hydrox 4-apatite
Outer diameter	0.5–3 mm
Wall thickness	<0.1–0.5 mm
Porosity	30–50%
Mean pore size	0.2 µm (Al ₂ O ₃), 0.2–0.7 mm (Si ₃ N ₄), 4nm (with γ-Al ₂ O ₃ coating)
<i>Performance</i>	
N ₂ permeability	$5 \times 10^{-8} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (Al ₂ O ₃)
Water permeability	> 500 l/nmbar (Al ₂ O ₃)
Burst pressure	up to 40 bar (Al ₂ O ₃), > 40 bar (Si ₃ N ₄)
Three-point bending strength	up to 170 MPa (Al ₂ O ₃), up to 450 MPa (Si ₃ N ₄)

In Table 3 some typical dimensions and properties of TNO hollow fibres are presented. Control of porosity can be obtained by the sintering aid used in fibre precursor for silicon nitride, while for alumina the firing temperature is the most important parameter for porosity control. If permselective properties are requested, these can be obtained by coating with a γ-alumina top layer. Recently, TNO claimed separation factors equal to the theoretical Knudsen separation factors (Smid et al., 1996). As the membranes can be used as carriers for toplayers, many of the existing techniques can be applied to realise selectivity, including high-temperature resistant polymer toplayers like polyimide ones.

It should be realised that ceramic hollow fibres are a relatively recent development which is still expected to undergo further improvements. As it stands now, TNO expects a final production price per square meter membrane area of at least one order of magnitude lower than that of membrane tubes. A major problem still to be solved is the creation of the connection of the ceramic material to the steel tubing of the rest of the plant. In the existing microfiltration ceramic membrane modules, polymer pottings are used but this limits the application to low temperatures. TNO also claims the invention of a ceramic potting/module system though information is proprietary (Brinkman, 1998). No significant progress has occurred since the early 1990s when multiple brazing techniques were optimised (Velterop, 1991). Such method is though very expensive so that remote cold sealing outside the hot region of the membrane module still remains a valid alternative despite the considerable space consumption it implies.

2.4. Reactor and transport modelling

Shifting finally to some modelling issues, several investigators have faced the problem of modelling of mem-

brane reactors either to achieve a proper interpretation of their experimental data or to assess the role of the various operating parameters (temperature, membrane permeability and permselectivity, feed flow rates and concentrations, etc.) on the performance of membrane reactors. In some other cases (e.g. Dixon et al., 1994), modelling studies helped to point the way towards experimental work concerning e.g. the need of more permeable or more stable membranes to outperform conventional technologies for given applications.

It has to be anticipated that most of these studies regarded rather simple reactor setup focusing on issues like type of flow patterns or role of sweep gas flow rate, meant for testing some opportunities at a laboratory scale rather than for large-scale industrial applications. When membrane reactors will gain penetration in the process industry, new models, much more complicated than those assembled until now will probably have to be solved. The review on models of membrane reactors written by Tsotsis et al. (1993) is recommended for a deeper insight in these topics. No dramatic improvements have appeared in the literature on the modelling of membrane reactors since then, with a few papers worth mentioning: Gockhale et al. (1995), Ziaka and Vasileiadis (1996) and Barbieri et al. (1997).

The need of governing properly heat balances in membrane reactors will certainly become a major task if large-scale industrial units will be ever put into operation. Being the performed reaction either endothermic (dehydrogenation) or exothermic (oxidation), innovative means to supply or remove heat from large-scale membrane reactor modules will have to be designed. In this context, the coupling of membranes and fluidised-bed reactors (Adris and Grace, 1997; Mleczko et al., 1996) seems to be particularly promising due to the superior temperature control potential of fluidised beds. The isothermicity assumption valid for several lab-scale membrane reactors will not hold anymore at large scale, and more complex modelling will have to be developed.

Waiting for industrial-scale membrane reactors, the most intriguing field in which modelling work still has to be done is that of transport through molecular-sieve membranes (Krishna and van den Broeke, 1995; Shelekin et al., 1995; Funke et al., 1997).

3. Selectivity enhancement

The improvement of reaction selectivity is a second field of application of membrane reactors on which most attention of the scientific community is nowadays addressed. In this context, considering consecutive reaction pathways, a permselective membrane could allow permeation of an intermediate product while rejecting either reactants or other undesired products (Fig. 1c). However, intermediate products (e.g. partially oxidised

hydrocarbons) are larger than the complete reaction products (e.g. CO_2) or the reactants themselves (e.g. O_2). This requires the imaginative use of some unconventional permeation mechanisms (e.g. capillary condensation, surface diffusion or multi-layer diffusion), which is rather complex and strongly depends on the particular reaction and membrane considered. For such a reason no interesting practical applications of this concept are known.

Another opportunity for the increase of the reaction selectivity lies in the controlled addition of a reactant along the reactor, through either a permselective or a non-permselective membrane (Fig. 1d). In fact, low oxygen or hydrogen concentrations in the reacting mixture are known to drive certain partial oxidations or hydrogenations to higher selectivities towards intermediate products (ten Elshof et al., 1995). Such low concentrations can be attained by dosing the key reactant (i.e. oxygen or hydrogen) at a desired rate through the membrane, which in this case might also be non-permselective (Coronas et al., 1995).

Contrary to conversion increase of equilibrium-limited reactions, the application of membrane reactors to selectivity enhancement of mostly partial oxidations (methane oxidation to syngas, oxidative coupling of methane, oxidative dehydrogenations, etc.), has been frequently investigated in the last couple of years. Hereafter, the prevalent obtained results are surveyed.

3.1. Methane to syngas conversion

A leading field of potential membrane reactor applications lies in methane to syngas conversion. In order to better evaluate the potential of membranes in this context a few words must be spent to analyse the current industrial technology. Fig. 3 shows the conventional two-step route to the syngas to be used for the pro-

duction of methanol. It is a rather well-established technology, highly integrated as concerns thermal energy management. It is based on a preliminary catalytic steam-reforming of methane, an endothermic operation leading to the conversion of part of the methane into CO and H_2 over Ni-based catalysts. The obtained gases then enter, at about 750°C , a second section where methane is oxidised non-catalytically by pure oxygen prior to a secondary reformer from which the final syngas composition is derived. The second step is generally called autothermal owing to the exothermicity of methane oxidation which is capable of sustaining the following reforming step leading to an outlet gas temperature of about 900°C . Heat is then recovered through several heat exchangers in series (e.g. to produce high pressure steam for electric energy production, to heat up boiler feed water, etc.) prior to a final compression of the syngas from about 45 bars to about 150 bars. Similar process schemes are employed for producing syngas for ammonia synthesis or the Fisher–Tropsch reaction. Despite the unfavourable reaction stoichiometry (increase in the number of gaseous molecules) reforming reactions are nowadays carried out at high pressures (up to 50 bars) for three main reasons:

- (1) the prevalent synthesis reactions are carried out at high pressure (generally above 30 bars); as a consequence, it is convenient to compress the reactants (methane, steam and oxygen) from ambient pressure up to the above pressure values rather than the syngas itself owing to the mentioned higher number of molecules;
- (2) the equipment volume is reduced, which is quite an advantage due to its high cost, entailed by the high temperature to be dealt with by constituting materials;
- (3) pressure drops per unit mass flow through the reformers are less at high pressure.

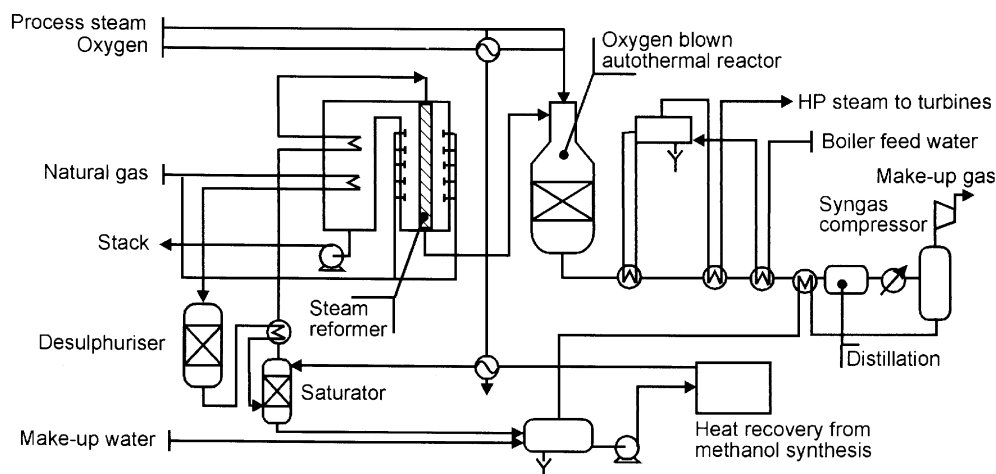


Fig. 3. Combined reforming for production of methanol synthesis gas.

Catalytic partial oxidation is much faster than reforming reactions, highly selective in a single reactor and even more energy efficient than the above process. It could thus in principle decrease significantly capital and operation costs of syngas production. This process, for which the most promising catalyst appears to be Rh-based ones, is though still at the R and D stage addressed in a joint effort by industrial and academic researchers (Bharadwaj and Schmidt, 1995).

If a ceramic membrane permselective towards oxygen (e.g. perovskite, yttria-stabilised-zirconia; Ma et al., 1996) could be used to dose this reactant to the catalytic bed for methane partial oxidation to syngas the below advantages could namely be attained:

- reactants are not premixed, which could lead to higher selectivities and less safety problems;
- the need of a preliminary cryogenic separation of oxygen from air could be offset since air could be fed to the catalyst-free side of the membrane, relying upon the permselectivity of this latter for nitrogen rejection;
- the process would be self-sustaining from the energetic viewpoint, the heat of reaction heating up the membrane to suitable temperature for oxygen transport (Bouwmeester and Burggraaf, 1997).

However, major drawbacks and difficulties have to be faced. For instance, air compression costs up to the syngas production levels (30–50 bars) may be too high owing to the need to compress uselessly nitrogen beyond the desired oxygen, although energy could be recovered by re-expanding the compressed nitrogen. However, if markedly different (tens of bars) pressures would have to be kept at opposite membrane sides, this would entail:

- extreme sensitivity to any membrane defect such as e.g. a crack, since through that defect large flow rates of methane would escape to the air side with potential explosion hazards;
- outstanding high-temperature sealings of membranes to modules would have to be employed to avoid leakages, which is quite a task as discussed earlier.

Further, according to the current literature the permeation rate through the best available membrane ($\text{SrFeCo}_{0.5}\text{O}_x$, Ma et al., 1996) is still relatively low compared to the reaction kinetics. Spatial velocities nowadays employed in pioneering studies (Balachandran et al., 1995, 1997; Mazanec, 1996; Tsai et al., 1997) are therefore somewhat lower than those envisaged for industrial application. Further some permeability loss has been observed for the mentioned promising $\text{SrFeCo}_{0.5}\text{O}_x$ membranes, probably ascribable to formation of strontium carbonates, if the studies by Bouwmeester and coworkers (ten Elshof et al., 1995) have to be taken as an indication. Despite the outlined difficulties the interest of the industrial world in this membrane process is serious. The developmental work has spawned the formation of two major academic-industrial consortia in 1997. Stimulated by the US Department of Energy a first consortium

was formed in May 1997 with the aim of developing through a 84 M\$ budget over 8 years, suitable membrane reactors for methane to syngas conversion with the final goal of producing liquid fuels. There are wide reserves of natural gas in remote gas fields, such as Alaska's North Slope and in off-shore locations, that cannot be exploited economically at present. If the gas could be converted in a liquid fuel the economics would change dramatically and the world's oil reserves would be boosted up by an equivalent 30 years consumption. Members of this consortium are Air Products and Chemicals, Babcock and Wilcox, Ceramtec, Eltron, Arco, Argonne National Laboratories, Pennsylvania State University and the University of Pennsylvania. At Argonne, Balachandran et al. (1995, 1997) studied methane conversion into syngas in a perovskite membrane reactor. Several membranes were employed, prepared as extruded tubes of perovskites belonging to the system La-Sr-Fe-Co-O and, in one case, of a non-perovskite mixed oxide ($\text{SrCo}_{0.5}\text{FeO}_x$). The membrane performance was strongly dependent on the perovskite stoichiometry which governs either the oxygen transfer rate or the membrane stability. In fact, perovskite-oxide tubes had a strong tendency to fracture as a consequence of the existence of an oxygen gradient inside the membranes (from the air-side to the methane-side) which introduces a volumetric lattice difference between the inner and outer walls (Pei et al., 1995). However, methane conversions higher than 98% (with 90% CO selectivity) were observed for $\text{SrCo}_{0.5}\text{FeO}_x$, when operating at 850°C by feeding air at the tube side and methane at the shell-side (where a Rh-based reforming catalyst was present); in this last case, some of the prepared tubes could withstand up to 1000 h operation without failure. The authors suggest that a reduction of the thickness of perovskite-based membranes would result in increased oxygen fluxes (thereby reducing the reactor volume) but also in higher membrane stability. In fact, the lattice oxygen involved in methane reforming, reacted away at the reaction side of the membrane, would be promptly replaced by new oxygen coming through the membrane itself, thereby preventing significant oxygen depletion in the perovskite lattice and reducing the risk of tube fracturing. However thin and defect-free supported perovskite membranes have still to be developed.

Similar objectives as those of researchers at Argonne are being pursued by a second consortium involving BP, Praxair, Amoco, Statoil and Sasol. Finally, it seems that a similar project will also start in Europe, funded in part by the European Community (Verweij, 1998). In this last case, the problem of sealing membranes into modules will probably be solved by producing very long membranes (12 m) quenched at both ends where polymeric gaskets will be employed. It is worth underlining that this represents a rather exceptional case in which the replication of lab-scale membrane properties is at least attempted at an industrial one.

By the way, direct oxidation of methane to methanol without passing through the syngas production step has also been attempted by using catalytic membrane reactors (Lu et al., 1996), though the improvements compared to conventional reactors were so poor that practical success can hardly be envisaged. The handling of methanol synthesis from CO_2 and H_2 below 200°C assisted by selective permeation of the produced methanol and water through perfluorinated Li-exchanged membranes appears to be definitely more promising (Struis et al., 1996).

3.2. Oxidative coupling

Another interesting reaction for membrane reactors, perhaps the most studied in the field of selectivity enhancement, is the oxidative coupling of methane. Lafarga et al. (1994) have recently developed a membrane reactor concept according to which an inert porous membrane is used to supply oxygen in a controlled way to a fixed bed of catalyst (Li/MgO) so as to drive methane oxidation to higher C_2 -selectivities. Competing reactions such as deeper oxidations are hindered by keeping rather low the oxygen average concentration along the entire reactor. The membrane they developed was based on a commercially available microporous alumina membrane having an average pore size of about $10\text{ }\mu\text{m}$. In order to control permeability, these researchers deposited silica in the membrane pores by dipping the membrane into silica sols, followed by calcination at 800°C . In a similar way they developed tubular membranes with a non-uniform permeation pattern along their axial length (Coronas et al., 1994b) so as to modulate the oxygen feed in each reactor section according to an optimum feeding strategy. The obtained results are rather encouraging: the reached yields (up to 23% in oxidative coupling products; Coronas et al., 1994a) are very close to the limits required to achieve commercialisation (i.e. 25–30%). A further yield increase might be achieved by suppressing the negative effect of the silica-alumina membrane acidity on the coupling reaction, by impregnating the membrane with alkaline (Li) or alkaline-earth (Mg) compounds (Herguido et al., 1995), as suggested on the grounds of a recent modelling study (Coronas et al., 1997b). Within the same research group in Zaragoza the oxidative coupling of butane was also studied getting further confirmations to the above findings (Tellez et al., 1997). Similar results were also obtained with similar membrane reactors by Ramachandra et al. (1996) and Tonkovich et al. (1996a). Less promising results were obtained by Borges et al. (1995) by use of a porous LaOCl membrane supported on a commercial alumina tube. The membrane was in this case intrinsically active. The highest C_2 yields (11.1%) were reached feeding O_2 and CH_4 at opposite membrane sides.

As concluded by Ramachandra et al. (1996), after studying the oxidative coupling of methane in a porous

Vycor-glass membrane reactor, potential improvements of the results obtained with porous membranes could be attained with dense membrane reactors where the dense membrane would prevent methane and hydrocarbon losses to the air-feed side, while at the same time permitting a significant flux of oxygen across the membrane (Lu et al., 1997; Guo et al., 1997). A number of papers have recently appeared in the literature dealing with dense membrane application to the oxidative coupling of methane, ranging from perovskite oxides (Balachandran et al., 1995; ten Elshof et al., 1995; Lin and Zeng, 1996) to stabilised zirconia (Hamakawa et al., 1997), from proton and oxide-ion conducting materials such as $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ or $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$ (Langguth et al., 1997) to doped bismuth oxide membranes (Zeng and Lin, 1997).

In this context, perovskite membranes (based on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$) similar to those used by Balachandran et al. (1995) in their earlier described work, were prepared by ten Elshof et al. (1995) in a disk-shape and tested for their activity in the oxidative coupling of methane. Permeation of oxygen through the membrane was kept high enough by operating above 800°C . No additional catalyst was used. Up to 70% selectivities towards C_2 compounds were detected, but at the price of lower than 3% methane conversions, when reactants were fed at opposite membrane sides. Membrane degradation phenomena similar to those described by Balachandran et al. (1995) were noticed in this case, too. Selectivity dropped down to 35% when reactants were premixed and fed together to one side of the reactor. This implies that the lattice oxygen driven through the membrane can improve the C_2 selectivity of the reaction taking place at the membrane surface exposed to the methane flow. This potential advantage should stimulate the efforts in trying to increase the membrane surface area per unit volume of the reactor, so as to increase the yields, which are now too low for practical application. However, the catalytic activity of perovskite oxides strongly depends on their nature, synthesis method, surface oxygen exchange rate and electronic conduction mechanism. For instance, Lin and Zeng (1996) showed how $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ is a quite active and selective membrane material towards the oxidative coupling in oxidising environments, whereas $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ is not. Zeng and Lin (1997) showed that Bi_2O_3 -based materials (e.g. $\text{Y}_2\text{O}_3/\text{Bi}_2\text{O}_3$, $\text{Er}_2\text{O}_3/\text{Bi}_2\text{O}_3$ or $\text{Nb}_2\text{O}_5/\text{Bi}_2\text{O}_3$) offer even better potential for membrane reactor application due to high activity towards methane coupling, even in reducing atmospheres.

3.3. Oxidative dehydrogenation

A further promising application field for membrane reactors is represented by oxidative dehydrogenation of hydrocarbons.

Coronas et al. (1995) applied the same reactor used for methane oxidative coupling (a fixed bed of Li/MgO catalyst encompassed by a porous membrane; Coronas et al., 1994a,b) to the oxidative dehydrogenation of ethane to ethylene. Oxygen was permeated through the membrane whereas ethane was fed axially. Ethane conversion higher than that of conventional pre-mixed feed reactors could be obtained, with good selectivity to ethylene and higher hydrocarbons (overall yield equal to 57%). According to the authors, as opposed to the oxidative coupling of methane, this feature has not to be attributed to kinetic effects linked to the comparatively low oxygen concentration in the first part of the reactor, but to a better heat management policy (no hot spots are formed because the heat of reaction is generated along the entire length of the reactor and not mainly close to its inlet). Tonkovich et al. (1996b), on the basis of the results of a very similar experimental work (ethane oxidative dehydrogenation to ethylene, on a Li/Sm–MgO catalyst, carried out with a porous alumina membrane fed at opposite sides with ethane and air), stated that the comparatively high ethylene yields they obtained (up to 51% against 8.1% of a conventional fixed-bed reactor with premixed feed of reactants) should also be due to the lower oxygen partial pressure allowed by the membrane reactor at the catalyst side. Both studies, however, stress that operation with the membrane reactor is safer compared to that of traditional reactors owing to the avoidance of any pre-mixing of reactants giving rise to explosive mixtures. In particular, Tonkovich et al. (1996b) noticed that periodic counter-propagating blue flames were present in some operating conditions in the conventional fixed-bed reactors, whereas no flames were observed in the membrane reactor. Further, Capannelli et al. (1996) compared the performance of a conventional packed-bed reactor to those of a monolithic one and of a catalytic membrane reactor with separate feed of reactants, in handling the oxidative dehydrogenation of propane over V_2O_5 - γ - Al_2O_3 catalyst: the membrane reactor gave superior turnover numbers and propylene selectivity, even though the difference with the monolith-type reactor was quite slight.

4. New emerging application opportunities

Although for many potential applications in reactors permselectivity is a prerequisite, for certain types of utilisation permselectivity is not requested or its function is reduced to a simple filtration operation; separating only particles instead of molecules. As permselectivity in the hostile, corrosive and often fouling or poisoning reactor conditions is often difficult to achieve or to maintain, non-permselective operations are easier to achieve and may pave the way to more sophisticated separation/reaction application in the future by producing the reactor concepts and module shaping. Moreover, a range of

potentially interesting non-permselective applications have recently been formulated and some of them have already been tested on a pilot-plant scale. These potential applications will be discussed below together with possible further developments.

4.1. The catalytic membrane reactor with separate feed of reactants

Fig. 4 illustrates the principle of the catalytic barrier membrane reactor, first proposed by van Swaaij and co-workers in the late 1980s for some environmental catalytic reactions (NO_x reduction with ammonia or SO_2 reaction with H_2S ; Slood, 1991). In this reactor the different reactants are fed separated at the two sides of a catalytically active membrane. Since the reaction rate is chosen higher than the transport rate inside the membrane, the reaction takes place in a small zone or a plane. Changing the reactant concentrations outside the membrane will result in shifting the position of the reaction plane to a new location where transport rates to the reaction plane are again matched by the reaction stoichiometry (Fig. 5a). This principle was also demonstrated experimentally by Slood (1991). Slip of a reactant through the membrane (e.g. NH_3 for NO_x reduction) can be thus avoided. Often, it is also desired that all products of the reaction are directed to one side of the membrane. This would be e.g. the case of sulphur production for the reaction on H_2S with SO_2 where the produced sulphur should be directed to the SO_2 side (Slood, 1991). By the application of an overpressure at one side of the membrane (Fig. 5b), due to the combined action of convective and diffusive flows this can be realised (see e.g. Slood, 1991; Saracco et al., 1995b; Neomagus et al., 1998). Further, by application of a pressure difference between the two opposite membrane sides, an increase of the yield of intermediate products of a series of consecutive reactions could be reached (Golman et al., 1997), because the

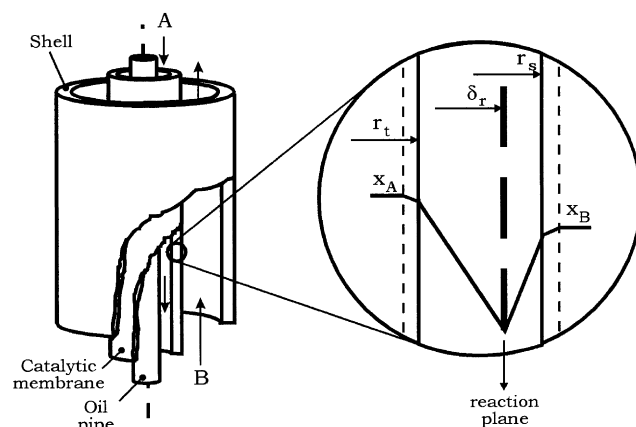


Fig. 4. Schematic representation of a catalytic membrane reactor with separate feed of reactants.

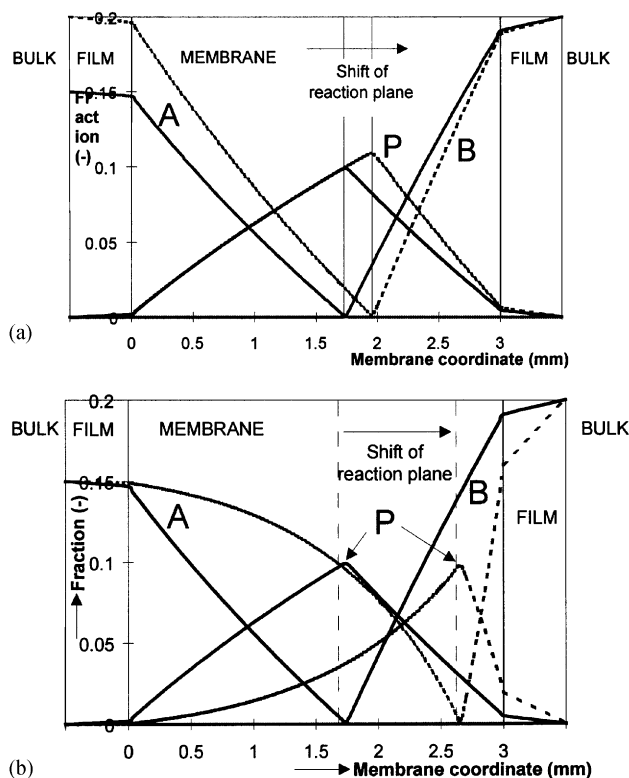


Fig. 5. Shift of reaction plane due to increase of reactant A (left; reaction $A + B \rightarrow P$) and due to introduction of pressure difference over the membrane (right).

trans-membrane convective flux generated would reduce the residence time of desired intermediate products (Neomagus et al., 1998).

The potential for carrying out highly exothermic reactions such as hydrocarbon combustion in a controlled way have been studied more recently (Veldsink, 1993; Saracco et al., 1995a, b, 1996b). Provided reaction kinetics are high enough compared with the transport rates the most peculiar features of this membrane reactor are: slip of reactants to opposite membrane sides are avoided; reactants are not premixed thereby avoiding formation of explosive mixtures; low sensitivity to thermal runaways (conversion rate is controlled by transport phenomena); there is a good flexibility and easy controllability (any change in reactant partial pressures in the gas feeds leads to a shift of the reaction zone inside the membrane) the per-pass conversion can be increased by application of a pressure gradient over the membrane which increases the inlet flux of a key reactant (fed at the high-pressure side).

Technically, it could be interesting to carry out combustion processes catalytically at low temperatures (say 500–600°C) to avoid NO_x production. To realise this type of operation e.g. ceramic combustion tubes are placed around steam pipes, while overpressure is put on the hydrocarbon side of the membrane to direct all com-

bustion products (CO_2 , H_2O) to the air/flue gas side. With support of the National Dutch Gas Institute GAS-TEC N.V. a lab-scale pilot plant based on this principle was operated (Veldsink, 1993) giving satisfactory results (Fig. 4). Some further intensification of the operation is still necessary to reduce the size of this type of combustors, but this does not seem to be an insurmountable obstacle. A more difficult problem is the sealing of the ceramic tubes and their connection to the metal tubes. In the pilot-plant spring below connections were used based on a multiple-brazing technique developed by Velterop BV, but for a large-scale multitubular furnace this is too expensive. Low-cost ceramic-to-metal sealing techniques are not yet available and localised cooling of the sealing places expensive. The problem could possibly be circumvented by the use of sintered metal tubes instead of ceramics (Neomagus et al., 1998). An additional advantage could be the somewhat higher heat conductivity of the sintered metal tube walls. Problems to be coped with are the higher permeability leading to smaller differential pressures over the membrane complicating the control and possibly the smaller thermostability of sintered metal in the requested temperature range. Nevertheless also here a shifting reaction zone operation and the direction of products for one side could be realised. Such properties could even be realised for thin layers of packed catalyst powder pressed between two porous barriers. Such a catalytic active membrane carrier has some advantages such as easy homogeneous distribution of catalytic activity and possibility of replacing the catalyst itself leaving the reactor intact. Fig. 6 demonstrates, on the grounds of a model based on the dusty-gas approach and for the simple CO oxidation, how the combustion products CO_2 is distributed between the two sides of the membrane as a function of the overpressure. By putting the over-pressure on the oxygen side of the membrane partial oxidations can be realised. The over-pressure would thus direct via convective flows the products to the hydrocarbon side where they are hindered from further oxidation.

The principle described here can be applied to syngas production where very high temperatures occur (say 800–1100°C) or to partial oxidation of more complex molecules at lower temperatures (250–500°C). As discussed earlier, both lines are presently under investigation at our group at the Twente University. Partial oxidation of methane to syngas using a catalyst is receiving presently a lot of attention because it can produce directly a product gas with a H_2/CO ratio of 2 requested for Fischer-Tropsch or methanol synthesis via an exothermic process. The direct route of mixing methane with oxygen and passing these gases at high temperature over a catalyst requires only an extremely short contact time allowing monolith reactors to be used. However premixing involves a substantial risk for large-scale equipment. It was shown by Alibrando et al. (1997) that

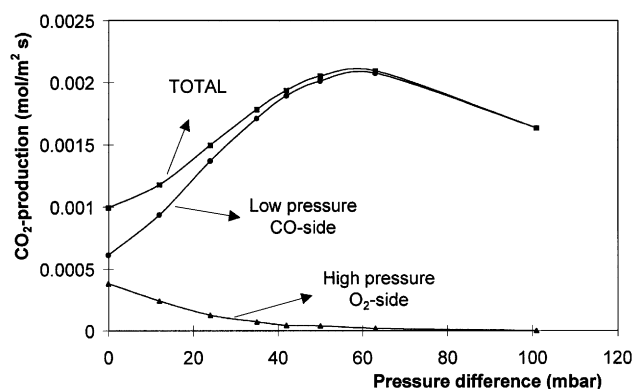


Fig. 6. CO₂ production by CO oxidation as a function of the pressure difference in a fixed bed barrier reactor.

the application of a ceramic membrane as a distributor of oxygen allowed a safe mixing of the two reactants, even at relative low methane-to-oxygen ratio with parallel conversions to syngas over a Rh/TiO₂ catalyst bed.

4.2. The barrier/condenser reactor

Another example of a non-permselective membrane reactor has been proposed by Hallon and Wajc (1994). Here the reactants are fed premixed at one side of the membrane while the product can be withdrawn in a liquid form via a condenser surrounding the catalytic barrier wall (Fig. 7). The function of the catalytic barrier wall is to provide the catalyst for the reaction, which can, in case of an equilibrium reaction, be operated close to optimal conditions. The principle was shown to work with a bench scale unit in which toluene was hydrogenated to produce methylcyclohexane as a test reaction. The concentration and temperature profiles shown in Fig. 7 were calculated by a specific model. These results show the potential of such multifunctional reactors. The main advantage lies in the absence of large recycle flows in the case of equilibrium reactions due to continuous product removal and possibly a higher reaction intensity. In most cases, a purge will nevertheless be required to remove by-products. The idea of Hallon and Wajc can be combined with the principle of separate reactant feeding to increase the selectivity of consecutive reactions of the type $A + B \rightarrow P + B \rightarrow X$ in which P is the desired product and X an undesired by product.

Finally, extremely interesting results in methane direct oxidation to methanol in a similar reactor concept to the one proposed by Hallon and Wajc (1994) were indeed obtained by Liu et al. (1996). The set-up used in the present study is depicted in Fig. 8. It consists of a tubular reactor with a small-diameter non-permselective membrane whose function was to provide an uniform flow distribution and to separate the hot reactor wall (heated by an external cylindrical oven) from the inner cooling

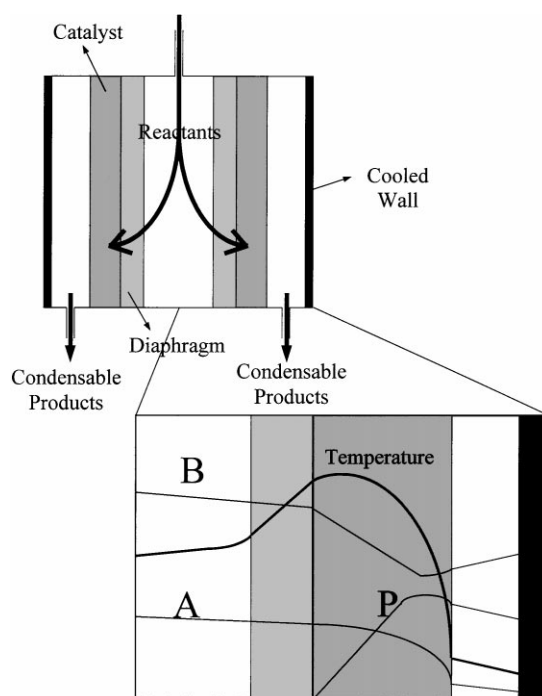


Fig. 7. The barrier/condenser reactor for carrying out a $A + B \rightarrow P$ reaction, being P a condensable product.

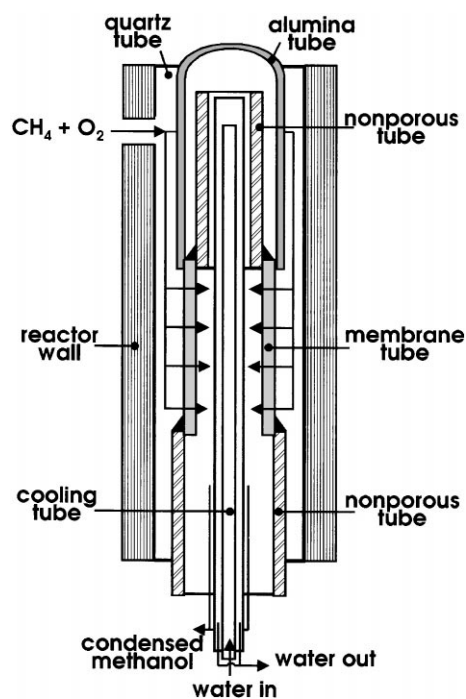


Fig. 8. Cross-section of the non-isothermal, non-permselective reactor (adapted from Liu et al., 1996). Radial scale enlarged for the sake of clarity.

tube, flushed with water, placed axially in the centre of the reactor. Such tube rapidly quenched the reaction zone preventing further reaction of methanol whose selectivity was therefore markedly enhanced at the operating

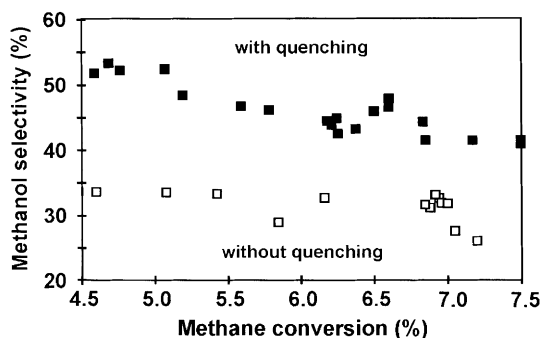


Fig. 9. Comparison of the performance of the reactor in Fig. 8 with and without quenching. Reaction conditions: pressure = 3.5 MPa, feed flow rate: $500 \text{ cm}^3 \text{ min}^{-1}$ (O_2 : 8%, CH_4 : balance), temperature of reactor wall = ca. 800 K (adapted from Liu et al., 1996).

conditions listed in the caption of Fig. 8. Fig. 9 shows the variation methanol selectivity against methane conversion in the presence and in the absence of quenching. The condensation effect is pushing methanol selectivity to the highest values (40–55%) ever measured in practice for the considered range of methane conversion (4–8%). What is even more surprising is that no catalyst was used in this innovative set-up. However, it should be stressed that these concepts have never been tried out in an integrated fashion and that problems may be insurmountable in practice.

4.3. Three-phase membrane reactors

A further example of using separated feeding towards a catalytic barrier is the three-phase membrane reactor with liquid reactants introduced at one side of the reactor and gaseous reactants at the other side. The aim is here to create a sustained interface between gas and liquid with a high specific area while allowing for heterogeneous catalytic activity. For gas–liquid contacting without heterogeneously catalysed reaction this concept already met with some success with polymer membranes (Kreulen et al., 1993) while TNO already operated a pilot plant. Because the momentum balance of gas and liquid phases are decoupled, countercurrent operation is possible without any risk of flooding. This is very important for hydrodesulphurisation of oil fractions, where in the usual co-current operation the increasing H_2S partial pressure, inhibits the reactions and frustrates attempts to produce lower concentrations of sulphur in the product. Further, especially because of the recent developments in the production of inorganic tubes of small diameters and the possibility of heat exchange in the liquid phase makes this type of reactor a possible alternative to trickle flow worthwhile to consider (Vitulli et al., 1997; Tilgner et al., 1997).

Cini and Harold (1991) predicted by model calculations an increase in the efficiency factor when perform-

ing the α -methyl styrene hydrogenation on a γ -alumina membrane. By applying a small pressure difference over the membrane, any liquid leakage could be avoided. As a consequence, the formation of a liquid film upon the catalytically active membrane was prevented, thereby reducing the related mass transfer resistance to the benefit of conversion. It was also argued, as proven more recently (Peureux et al., 1995), that this reactor can be particularly suitable for fast volatile-reactant limited reactions, since the gaseous reactant cannot be limiting any longer, contrary to conventional reactors.

4.4. The filtering slurry reactor and the fluid bed filter reactor

The filtering slurry reactor is yet another example of a reactor with membranes non selective on a molecular scale. The principle is given in Fig. 10. In many cases a slurry reactor has several advantages as a three-phase reactor over trickle flow. Smaller particles can be used to avoid diffusion limitation, heat transfer and uniform temperature operation and easy particle replacement. However, particle removal from the product and recycling of the catalyst to the reactor can be very difficult especially for high-pressure operation. Moreover, in a slurry reactor the liquid phase is mostly well mixed which can be a disadvantage if high conversions are requested. By installing sufficient membrane area in the slurry reactor the filtration can be carried out inside the reactor thus avoiding catalyst handling. In most cases the requested filtering area is relative small as due to the stirring action of the bubble filter cake built up can be avoided. Huizenga et al. (1995) showed that the occurrence of cake built-up can be described by a single dimensionless number, called the cake built up number.

For biological systems this reactor principle has already been demonstrated on commercial scale and there seem to be no reason why this cannot be applied to other slurry systems like hydrogenation or desulphurisation. In fact, patent literature claims this filtering membrane reactor for Fischer–Tropsch slurry syntheses. Staging can also be introduced by installing different filtering compartments in which case even the catalyst composition can be changed along the reaction path.

Introducing membrane areas in a gas–solid fluid bed for removal or addition of reactants or products seems to be particular interesting as in these type of reactors also the handling of the heat of reaction is relatively easy. Some of the principles explained earlier in this paper could also be carried out in a fluid bed system to combine the advantages of the membrane with the ease of heat removal/addition of a fluid bed.

Grace and coworkers (Adris and Grace, 1997) demonstrated the concept of the fluid bed membrane reactor for the steam methane conversion. In this reactor permselective palladium top layered membrane tubes were used to

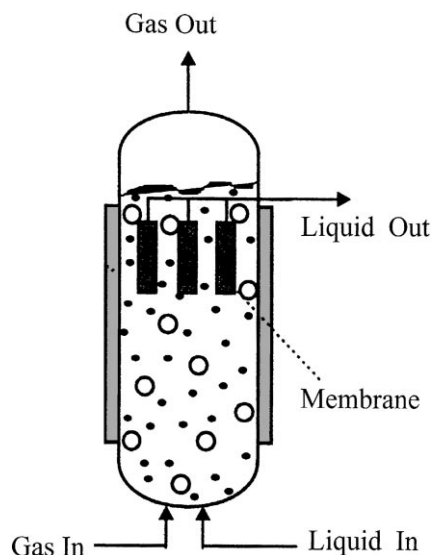


Fig. 10. Scheme of the filtering reactor.

withdraw pure hydrogen from the bed. Mleczko and co-workers (Mleczko et al., 1996) studied fluid bed membrane reactors for catalytic partial oxidation of methane to synthesis gas. In such reactors permselective membranes are used but non-permselective membranes could also be helpful to introduce reactants (e.g. oxygen) at a low concentration, without bubble formation which could produce an excessive amount of combustion products by homogeneous combustion.

3.5. Catalytic filters for simultaneous removal of fly-ash and noxious gases

Consider a porous barrier, made of a material (ceramic or metallic) capable of withstanding those temperatures which are generally required by gas–solid catalytic processes ($>200^{\circ}\text{C}$) and having a pore size small enough to prevent efficiently fly-ashes from passing through. Such barrier can be catalytically activated, by deposition onto its pore walls of a suitable catalyst, obtained with proper heat treatments once the basic structure has been impregnated with appropriate precursors (sols, concentrated solutions, etc.). The obtained product would become a particular type of catalytic reactor, suitable for simultaneous removal of fly-ash and noxious gases.

The idea of coupling catalysts for NO_x reduction and high-temperature resistant fly-ash catalytic filters (pore sizes: 30–100 μm ; Fig. 11a) in the treatment of flue gases from a coal burner, is very recent (Kudlac et al., 1992). Such filters were applied directly on the hot flue gases after SO_2 abatement by dry scrubbing, and before the air pre-heater. The technology of non-catalytic ceramic filters is nowadays well developed. A number of interna-

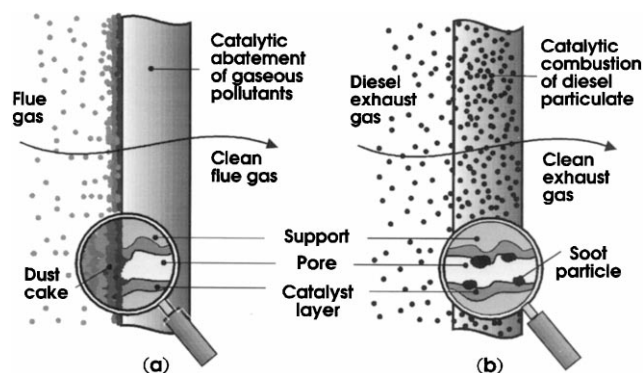


Fig. 11. Applications of catalytically active porous barriers as: (a) catalytic filter for simultaneous removal of gaseous pollutants and fly-ash; (b) catalytic trap for diesel particulate abatement.

tional companies (e.g. 3M, Corning, Schumacher, etc.) produce and install ceramic filters for high-temperature dust removal employing either rigid (sintered grains of SiC , mullite, etc.) or flexible filter-media (ceramic or metallic fibrous yarns), which generally operate through a cake-filtration mechanism with periodic jet-pulse cleaning (Clift and Seville, 1993). Once activated with suitable catalytic species, such filters might separate fly-ashes and catalytically abate gaseous pollutants (e.g. NO_x , volatile organic compounds) passing through the intimate structure of the filter. These catalytic filters might be applied in the treatment of flue gases from coal-fired burners, waste incinerators, etc. (Saracco and Specchia, 1998a).

Earlier studies of ours in this field concerned the development of suitable techniques for intruding a $\gamma\text{-Al}_2\text{O}_3$ layer on the pore walls of the filters and the preparation of filters modified with some of the above techniques (Saracco and Montanaro, 1995a, b), and pilot-plant studies, demonstrating the feasibility of the catalytic-filter concept, in which 2-propanol dehydration to propylene (catalysed by the transition alumina itself with no need of further catalytic principles) was used to simulate the abatement of gaseous pollutants (Saracco and Specchia, 1995a, b). Current work is focused on the synthesis, characterisation and pilot-plant testing of $\text{V}_2\text{O}_5 \cdot \text{Al}_2\text{O}_3$ - (Saracco et al., 1996) and $\text{V}_2\text{O}_5 \cdot \text{TiO}_2$ -deposited ceramic filters (Saracco and Specchia, 1998c) for NO_x reduction with NH_3 . Preliminary results demonstrate that nearly complete conversion of nitrogen oxides can be obtained with negligible ammonia slip and N_2O production, when operating at optimal temperatures. Such optimal temperatures strongly depend on the catalyst type, the $\text{V}_2\text{O}_5 \cdot \text{TiO}_2$ catalyst being more suitable in the range $200\text{--}300^{\circ}\text{C}$, the $\text{V}_2\text{O}_5 \cdot \gamma\text{-Al}_2\text{O}_3$ one for temperatures higher than $350\text{--}420^{\circ}\text{C}$ (Fig. 12).

Pina et al. (1997) in a recent series of papers addressed the catalytic combustion of VOCs through supported $\text{Pt-Al}_2\text{O}_3$ catalytic membranes having pore-size (few

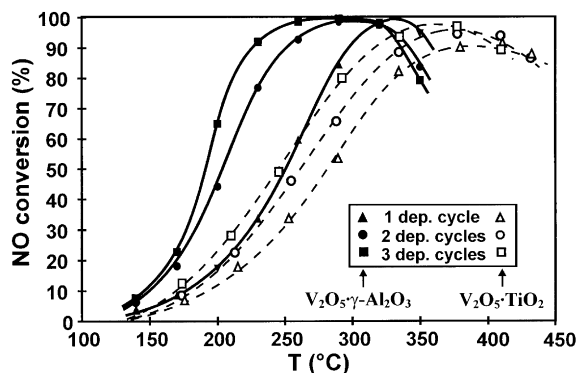


Fig. 12. NO abatement efficiency by SCR with ammonia through catalytic filters, activated via a different number of catalyst deposition cycles of two different catalysts: $V_2O_5\text{-}\gamma\text{-Al}_2O_3$ and $V_2O_5\text{-TiO}_2$. Superficial velocity = 16 m h^{-1} . NO and NH_3 feed concentration = 1800 ppm. Data from Saracco et al. (1996) and Saracco and Specchia (1998c).

nano-meters) falling in the Knudsen regime. Since in the Knudsen regime the probability of collision between molecules and pore walls is maximised compared to Poiseuille flow, this reactor was expected to give higher efficiency at low temperatures than rather conventional honeycomb catalysts in the abatement of VOCs from rather diluted streams as those commonly encountered in practice. This expectation was completely fulfilled, at the price, however, of very high-pressure drops through the catalytic barriers for superficial feed velocities of industrial interest. The pressure drop measured under reaction conditions (operating pressure: 1 bar, operating temperature: $130\text{--}200^\circ\text{C}$) ranged from 0.18 to 0.35 bar for superficial velocities between 3.5 and 7 m/h. This implies such high pumping costs to outset the feasibility of the process. Conversely, the membrane area for a given gas flow rate to be treated could in principle be increased, but the investment cost would probably affect the economic balance. Likely, unless extremely thin supported membranes are produced, thereby enhancing permeability of at least 1 order of magnitude, this promising idea will not express its industrial potential.

4.6. Catalytic traps for diesel particulate control

The combustion processes occurring in Diesel engines are often incomplete, and undesirable by-products are formed owing to the effect of uneven fuel-to-air mixing within the combustion chamber. In this context, diesel particulate (a mixture of soot aggregates carrying adsorbed hydrocarbons, sulfates and metal oxides) is raising a special health concern due to its carcinogenicity. Nowadays, no technique is capable of abating satisfactorily such particulate, and considerable improvements have to be made so as to cope, in the near future, with more and

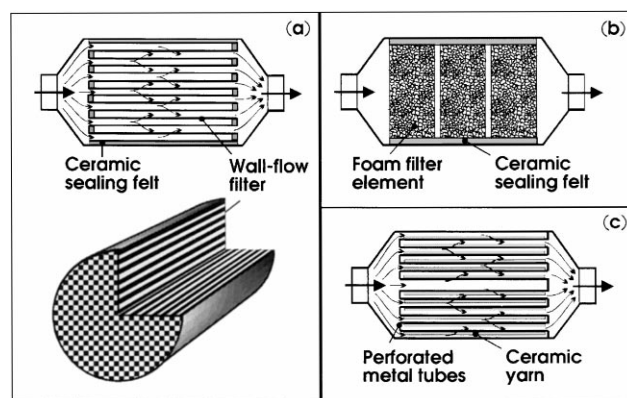


Fig. 13. Diesel particulate traps for car exhausts: (a) wall-flow monolith, (b) foam filter; (c) fiber filter.

more severe law restrictions. One of the potential ways to solve the problem of diesel particulate emission from either stationary or mobile sources is the use of traps carrying a suitable catalyst for promoting particulate combustion as soon as it is filtered. Fig. 11b shows the scheme of a catalytic trap for diesel soot removal, whereas Fig. 13 shows the different kinds of traps that have been proposed and tested for the mentioned purpose. A monolithic wall-flow filter, whose operation principle is enlightened in Fig. 13a, is a shallow bed filtration device, not that suitable for enabling a good contact between the filtered particulate and the deposited catalyst; conversely, wire mesh or fibre filter (Fig. 13b) and ceramic foams (Fig. 13c) act as deep bed filtration devices. Since in a catalytically coated trap the contact between soot and catalyst mainly depends upon the geometrical surface of the catalyst itself, the design of a support which guarantees good contact conditions between particulate and soot is very important.

In a pioneering work, Watabe et al. (1983) first demonstrated how the use of a catalyst placed on the pore walls of a ceramic foam trap could reduce remarkably the pressure drops across the trap, eventually leading, as opposed to a non catalytic trap, to a stationary pressure drop. Such steady state condition is related to a precise particulate hold-up, arising from the balance between the particulate trapped through a number of filtration mechanisms (inertial impaction, interception, brownian diffusion, etc.) and the particulate burned catalytically.

A lot of work has been recently carried out, or is in store, as concerns the choice of active enough catalysts (catalytic combustion should take place at the actual diesel exhaust temperatures, i.e. $150\text{--}500^\circ\text{C}$); the deposition of such catalysts on suitable filter media (e.g. sintered ceramics, ceramic foams or tissues); the thermochemical stability of the catalyst and the trap, etc. The stability and the reaction mechanism of a Cu-K-V-based catalyst, one of the most active ever proposed (Watabe

et al., 1983), were recently investigated as well as new catalysts based on mixtures of vanadates and chlorides (Serra et al., 1996; Saracco et al., 1997; Badini et al., 1998). Such catalysts can generate low-temperature eutectic liquids which wet the soot particles thereby improving the contact conditions between catalyst and carbon, meanwhile favouring the catalytic combustion via redox mechanisms mostly governed by vanadates. However, this unique feature also implies catalyst stability problems (evaporation, liquid migration inside the trap, ...) which are under investigation.

5. Conclusions

The interest in application of high-temperature (ceramic) membrane reactors is still growing. A shift in attention can be noticed from improving of equilibrium limited reactions via membrane separation of one of the products, towards selectivity increase and dosing of reactants via membranes. Attempts to improve permselectivity have been undertaken for all types of the membranes applicable in high-temperature reactors. Special progress was noted in the production of amorphous silica topayers, layers of zeolites and a creeping improvement of dense metal membrane topayers. Remaining problems for silica topayers are stability towards steam, layer adhesion, larger scale production and production costs. In the case of zeolites large-scale production of defect free layers for zeolites with smaller pores than silicalites is an important target.

Progress was noticed in oxide membranes (perovskite type), with mixed ion/electron conduction. For a lab-scale production of syngas from methane and air, in which only oxygen permeation takes place, high oxygen fluxes were reported in combination with high selectivity and conversion, almost suitable for industrial production conditions. The membranes were found to be stable over a period of more than 1 month. Nevertheless, problems like mechanical stability remain to be solved. The strong interaction with supports, if applicable at all, may hamper the use of thinner layers. Another important expected breakthrough are ceramic hollow fibres, with interesting mechanical and physico-chemical properties, that were produced, allowing to create ceramic membrane modules with high specific areas. As regards sealing and module building progress was lower.

Also for non-permselective membranes several new applications and innovative reactor configurations have been identified: membrane reactors with separate feed-stock, membrane reactors with condensing products, three phase membrane reactors, gas phase filter reactors, diesel exhaust soot converters and fluid bed membrane reactors. As currently available membranes can be used, these applications may pave the way to more sophisticated (permselective) membrane reactors.

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